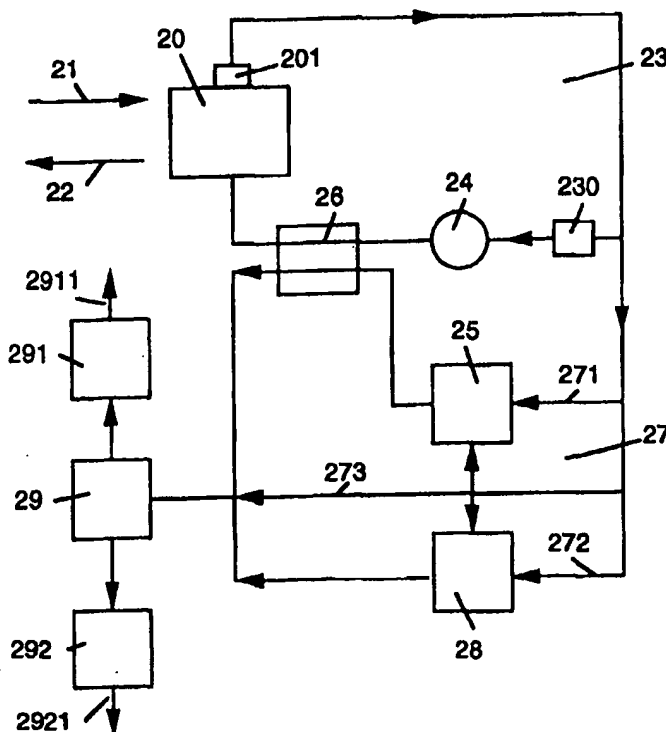




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SE98/01395 <b>(22) International Filing Date:</b> 16 July 1998 (16.07.98) <b>(30) Priority Data:</b> 9702750-2                      18 July 1997 (18.07.97)                      SE <b>(71) Applicant (for all designated States except US):</b> MELLIN, Monica [SE/SE]; Birkagatan 28, S-113 39 Stockholm (SE). <b>(71)(72) Applicants and Inventors:</b> MELLIN, Torgny, A. [SE/SE]; Birkagatan 28, S-113 39 Stockholm (SE). JENSEN, Kjeld [SE/SE]; Skogsängsvägen 13, S-141 43 Huddinge (SE). <b>(74) Agents:</b> NILSSON, Karl et al.; Stenhagen Patentbyrå AB, P.O. Box 4630, S-116 91 Stockholm (SE).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Swedish).</i>
<b>(54) Title:</b> A PROCESS FOR SEPARATING A CONTAMINATING SUBSTANCE FROM A MATERIAL CONTAMINATED BY SAID SUBSTANCE		
<b>(57) Abstract</b>  A method of separating a contaminating substance, e.g. PCB, mercury, from a material contaminated with said contaminating substance, e.g. soil. The method involves heating the contaminated material in a first separation process and treating said material with a recirculating gas which is caused to pass repeatedly through the material in a closed circuit, a main loop (23), during the process while increasing in temperature to the boiling point of the contaminating substance present in said material, so that said contaminating substance will be successively expelled from the material and enriched in vapour phase in the recirculating gas. The expelled and enriched contaminating substance is separated from the gas in a second separation process carried out in a sub-flow loop (27). Any thermal energy that is released during the second separation process is returned to the closed circuit (23) and therewith supplied to the first separation process.		



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A PROCESS FOR SEPARATING A CONTAMINATING SUBSTANCE FROM A MATERIAL CONTAMINATED BY SAID SUBSTANCE

FIELD OF INVENTION

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The present invention relates to a method of separating a contaminating substance from a material contaminated with said substance. Examples of such contaminating substances are chemical substances, such as PCB, dioxins, aliphatic and aromatic substances in creosote, oil and other petroleum compounds, and other chemical substances that have similar chemical and physical properties as the first-mentioned chemical substances, and distillable metals such as mercury and distillable compounds of such metals. Examples of contaminated materials are soil, sediments, sludge, land-fill materials, etc.

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BACKGROUND OF THE INVENTION

A general application of the invention exists in the industrial separation of such chemical substances from a material that contains these substances. A practical and environmentally addressed application of the invention is the decontamination of soil, sediments, sludge, land-fill materials, etc., that are contaminated with such chemical substances. The invention is described in the following with reference to this application thereof.

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Methods for separating organic or inorganic substances from contaminated materials are known to the art. Many different decontamination methods are also known, all of which have their advantages and disadvantages. High temperature combus-

30

tion, dumping, biotechnical (microbial) methods, chemical extraction and thermal expulsion are the main types of methods used in this respect.

5     Combustion is a method normally applied with regard to small volumes of material transported to the incinerating plant, which is normally stationary. The material is either combusted directly at high temperatures or is heated to a temperature above the boiling point of the contaminating substances so as to vaporise said substances, whereafter the  
10     gaseous substances are led into a high temperature furnace for destruction, in a second stage of the decontamination process. The method is expensive, among other things because of the comprehensive purification process to which the flue-gases must be subjected. Furthermore, other toxic substances  
15     (chlorinated dibenzofuranes, dioxins) are liable to form if combustion of the contaminating substances is incomplete.

Dumping is a method that is often used despite the fact that  
20     it does not solve the contamination problem, but merely puts off the problem for future generations to deal with. Environmental poisons present in such dumps, landfills, will gradually leak into surrounding ground, water and air. The regulations concerning dumping have become more stringent in recent  
25     years, for instance in the U.S.A. and Germany. These regulations in combination with dumping fees will make dumping a less attractive alternative to those decontamination methods whose aim is to deal finally with contamination problems.

30     Research and development of decontamination methods based on biotechnology is being undertaken to a significant extent in Germany and the U.S.A., among other countries. Great expecta-

tions have been placed, and are placed, on these methods. However, successes have been limited hitherto. The naturally occurring bacteria used have difficulty in breaking down the heavier aromatic components in, e.g., creosote; certain components present are toxic to microorganisms in particular, hence the use of creosote as a wood preservative. Recent research, however, indicates that anaerobic bacteria, i.e. bacteria that live in an oxygen-free environment, are able to break down such substances. There is therefore no doubt that effective and bacteria-based decontamination processes will be used in the future, although probably in large, closed containers that enclose an oxygen-free environment and over long periods of time and with constant treatment (temperature adjustment, loosening, addition of nutrients, etc.). The costs involved will therefore be significant.

A fourth category of decontamination methods is the extraction of said chemical substances with a solvent (extraction agent), or washing of material with different types of detergent. In the former case, the contaminated material is mixed with solvent, wherewith the contaminating substances are transferred to and enriched in the solvent. The method has been applied in a variety of ways for some years in Denmark and Germany, among other countries. The cost involved can vary, depending on the type of material concerned, its water content, and the type and concentration of the contaminants involved, among other things. The suitability of these methods, particularly the washing methods, is greatly limited when the contaminated material is fine-grained, i.e. contains clay.

A fifth category comprises thermal expulsion, with or without subsequent combustion of the expelled contaminants. The present invention falls in this category.

5 German Patent Specification 4303722, for instance, describes a method of expelling contaminating substances from, e.g., contaminated soil in a furnace with the aid of heated steam or hot gas that contains an oxidant, wherewith the soil is freed from contaminating organic substances by direct oxida-  
10 tion of said substances in the material. It is said that some of the substances are not oxidised in the material, but are expelled and oxidised in a catalyst by catalytic oxidation, or in a UV-filter. 80-90% of the steam or hot gas is returned to the furnace. 10-20% of the steam/the hot gas is removed  
15 for condensation, whereafter the remainder of non-oxidising substances are extracted conventionally from the water condensate.

An oxidant that contains oxygen is thus added with the supply  
20 of steam/hot gas. The purpose is for the oxidant to be passed with the steam/hot gas through the material and therewith oxidise organic components present therein, including organic contaminants. Enrichment of the expelled contaminating substances is counteracted consciously, by continuously adding  
25 oxidants. Surplus oxygen is present in the steam or the hot gas subsequent to its passage through the material, partly as a rest and partly in the form of a fresh supply, and consequently said 80-90% of the steam/hot gas + oxidant is recycled to the material.

30

The main flow from the furnace passes through a catalyst or through a UV-filter, therewith oxidising the expelled con-

taminants. A sub-flow, 10-20%, is taken out continuously for condensation, followed by purification of the resultant water condensate. Thus, certain contaminating substances are oxidised in the material by the oxidant delivered with the steam or the hot gas, whereas other substances are driven-off and oxidised either by the catalyst or the UV-filter, or are extracted from the water condensate with conventional methods after condensation of the steam/hot gas.

10 This known method has a number of drawbacks. One drawback is that contaminated material will often contain significant proportions of organic components, humus substances, wood fibres, etc., which consume the oxidant introduced into the system. Consequently, large quantities of oxidant may be required, therewith adding to the costs.

Another drawback is that when 80-90% of the decomposition products are recycled to the material and when chlorinated substances are present and oxidised, the carbon dioxide, water (steam) and chlorine compounds formed will also be returned to the material, resulting in continuous corrosion of the plant, since chlorine is particularly corrosive.

A third drawback is the risk of igniting the material and of gas explosion respectively. According to the described method, the steam/hot gas contains a surplus of oxygen. There is thus a danger that the organic constituents of the material, not only the contaminating substances, will be ignited as a result of the combination of oxidizable organic substances, oxygen gas and high process temperatures (up to 700°C according to the text). There is also a danger of the formation of a hot and explosive mixture of gaseous contami-

nants and oxygen when the mixture exceeds the critical so called LEL levels (lower explosive limit) of such substances. The method is therefore hazardous, partly because the organic constituents of the material can catch fire in the furnace,  
5 and partly because of the risk of explosion, due to the explosive nature of the gas mixtures in the process plant.

It is also known that a chemical substance can be separated from a material that contains this substance, by treating the  
10 material with steam in a first stage, so as to expel the chemical substance from the material with steam; see U.S. Patent Specification 5,172,709. However, this known method involves condensing the steam directly with the chemical substance prior to extracting the chemical substance from the  
15 water in a second stage. This method, however, has been found to have certain drawbacks of a technical and economic nature.

The object of the present invention is, among other things, to eliminate the aforesaid drawbacks and to provide a cost-effective separation method for industrial application, including ground decontamination, which is adapted to and utilizes the advantages of both so-called co-distillation with water and steam distillation, and which, at the same time, is highly adapted to and utilizes the special chemical and  
25 physical properties of the chemical substances present in the material being treated.

#### DEFINITIONS

30 Hereinafter, the chemical substances in materials that contain these substances are designated as "contaminating substances" or "polluting substances" where such designation



is warranted according to definition, i.e. when such substances are classified as harmful to the environment in the application of ground decontamination as chosen here to describe the invention.

By co-distillation with water is meant that water is vaporised, which means that different contaminants or pollutants can be evaporated together with the water at the boiling point of said water by virtue of the co-distillation principle, even if the steam pressure of the contaminants or pollutants is particularly low at this temperature and the boiling point thereof is much higher than the boiling point of water. By steam distillation is meant that the material is treated with superheated steam, which expels the contaminants or pollutants. By "contaminated material" is meant soil, sediment, land-fill materials, etc., that contain contaminating substances.

The same applies in other applications of the invention, such as in certain industrial processes where separation of the chemical substances mentioned in the introduction from a material, solid or liquid, is desired.

## SUMMARY OF THE INVENTION

The inventive method involves heating the contaminated material in a first separation process and treating said material at a temperature up to the boiling point of the contaminating substance present with recycled gas which is caused to pass through the material a large number of times in a closed circuit during the process while increasing in

temperature, so that contaminating substances present in the material will be expelled successively therefrom and enriched in vapour phase in the recirculating gas.

- 5     The expelled and enriched contaminating substance is separated from the gas in a second separation process in a sub-flow loop, wherewith any energy released is returned to the closed circuit and therewith passed to the first separation process.

10

The separated contaminating substance can be separated from the gas in one of the following three ways, or in different combinations thereof:

- 15     1.    Enriched contaminating substance is separated from the gas by combustion in a burner and/or in a catalyst, wherein the thermal energy generated is passed back to the first separation process with the aid of a heat exchanger.
- 20     2.    Enriched contaminating, or polluting, substance is extracted from the gas, by cooling the gas and contaminating substance, whereafter water condensate and non-condensable gases respectively are cleansed of contaminating substance in a conventional manner, for instance by sorption in chemical
- 25     filters (activated carbon).
- 30     3.    Enriched contaminating, or polluting, substance is separated from the gas with the aid of a contaminant-selective chemical substance, either a substance (a so-called sorbent) which is chosen and adapted for complete or partial sorption and binding of the contaminating substance directly from the gas, or a substance which is chosen and adapted for

some other chemical reaction of the contaminating substance directly from the gas, e.g. chemical precipitation.

These and other characteristic features of the inventive  
5 method will be apparent from the following Claims.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in more detail with  
10 reference to the accompanying drawings, in which  
Fig. 1 is a diagrammatic illustration of the process of  
expulsion of a number of contaminating, or polluting,  
substances A-E as a function of process temperature ( $^{\circ}\text{C}$ ) and  
process time (t), whereas

15

Figs. 2-6 are schematic illustrations of the inventive  
process.

Fig. 2 is an explanatory sketch of the process and shows a  
20 main loop 23 which includes a process container 20 having a  
particle filter 201, a contaminated material inlet 21, a  
treated material outlet 22, a water injector 230, a fan or  
blower 24, and a heating unit in the form of a heat exchanger  
26.

25

Extending from the main loop 23 is a sub-flow loop 27 which  
comprises a part-loop 271 that includes a combustion unit 25,  
in the form of a burner and/or a catalyst, which is connected  
to the heating unit 26, and also a part-loop 272 that  
30 includes a unit 28 which contains a contaminant-selective  
chemical substance.

Both of the part-loops connect with a sub-flow loop 273 that includes a gas-cooling and gas-condensing unit 29 which, in turn, is connected to a unit 291 that includes a chemical filter for purifying the water condensate formed, and a unit  
5 292 which includes a chemical filter for purifying non-condensable gas. The sub-flow loop 27 departing from the main flow loop is also connected directly to said gas-cooling and gas-condensing unit. Purified water condensate is obtained at an outlet 2911 and passed back to the treated material, while  
10 purified non-condensable gas is obtained at an outlet 2921 for release to the surrounding atmosphere.

Fig. 3 illustrates the main loop 23 of Fig. 2 and the sub-flow loop 271 which includes the combustion unit 25 connected  
15 to the gas-cooling and gas-condensing unit 29, and from there to respective units for purifying the water condensate 291 formed and for purifying non-condensable gas 292. The purified water condensate is obtained at an outlet 2911 and passed back to treated material, while purified non-  
20 condensable gas is obtained at an outlet 2921 for release to the surrounding atmosphere.

Fig. 4 illustrates the main loop 23 of Fig. 2 and the sub-flow loop 273 which connects directly with the gas-cooling  
25 and gas-condensing unit 29 and from there to the water condensate purifying unit 291 and the non-condensable gas purifying unit 292 respectively. Purified water condensate is obtained at an outlet 2911 and passed back to the treated material, while purified non-condensable gas is obtained at  
30 an outlet 2921 for release to the surrounding atmosphere.

Fig. 5 illustrates the main loop 23 of Fig. 2 and the sub-flow loop 272 which includes the unit 28 that contains a contaminant-selective chemical substance, connected to the gas-cooling and gas-condensing unit 29 and from there to the  
5 respective units 291 and 292 for purifying water condensate and non-condensable gas. The purified water condensate is obtained at an outlet 2911 and passed back to the treated material, while purified non-condensable gas is obtained at an outlet 2921 for release to the surrounding atmosphere.

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Finally, Fig. 6 illustrates the main loop 23 of Fig. 2 and the sub-flow loop 271 that includes the combustion unit 25, and the sub-flow loop 272 that includes the unit 28 that contains a contaminate-selective chemical substance. Both of  
15 these units are connected to each other and also to the gas-cooling and gas-condensing unit 29 and from there to the units 291 and 292 for purifying the formed water condensate and the non-condensable gas respectively. The purified water condensate is obtained at an outlet 2911 and is passed back  
20 to the treated material, whereas purified non-condensable gas is obtained at an outlet 2921 for release to the surrounding atmosphere.

#### DETAILED DESCRIPTION OF THE INVENTION

25

##### First separation process

30

Contaminated material is treated in a first separation process with gas, air or an inert gas which is replaced successively with steam, therewith expelling the  
contaminating, or polluting, substances present from the contaminated material in vapour phase. Each substance present

in the gas is therewith enriched individually in accordance with Dalton's law, regardless of other substances that are expelled at the same time. Because the gas is recirculated through the contaminated material a large number of times in  
5 a closed circuit during the process, each substance will be enriched successively in the gas.

The contaminating substances present in the material are expelled, or driven-off, as a result of successively  
10 increasing the process temperature, i.e. the temperature of the contaminated material (providing, of course, that the contaminating substances have the requisite vapour pressure at the process temperature in question; metals, such as lead, copper, etc., cannot therefore be separated-out or extracted  
15 with this method).

As a result of this procedure, the gas will contain a surprisingly high concentration of respective substances expelled from the material. The expelled substances accompany  
20 the gas around the circuit and back through said material without being re-condensed (providing that the temperature of the gas does not fall below the temperature required to expel the substances) whilst more of the contaminating substance is continuously driven-off from the material into the steam.

25 Enrichment of the substances continues until a state of equilibrium is reached, so-called "saturation". Since different substances have different vapour pressures and are initially present in the material in greatly varying  
30 concentrations, the substances will be driven-off and enriched in the gas to varying degrees. Some substances (e.g. low-boiling point substances) will quickly reach this state

of equilibrium, whereas other substances (high-boiling point substances) will not even reach the vicinity of their respective "saturation contents" in the gas, due to their low vapour pressures and/or low initial concentrations.

5

Expulsion of contaminating substances in the first separation process can be facilitated by adding a chemical substance to the contaminated material either prior to or during the first separation process.

10

The contaminated material is heated with through-flowing and hot recirculating air or inert gas in a closed circuit, here referred to as the main loop 23. As the temperature of the material increases, moisture present in the material begins to vaporise and mix with recirculating air or inert gas.

15

Those contaminating substances present in the material and having a low molecular weight and low boiling point will begin to vaporise and admix with and be enriched in the air or inert gas. The temperature of the material is increased by heating the air or the inert gas prior to its recirculation to the material in the main loop.

20

As the temperature of the material approaches the boiling point of water, a rapidly increasing amount of steam (vapour) is delivered to the recirculating and heated air or inert gas. This results in an increase in the gas volume in the main flow. This increasing gas volume, air or inert gas and steam, is taken from the main loop into a sub-flow loop 27.

25

Thus, the composition of the recirculating gas in the main loop is changed successively from air or inert gas to steam with increasing process-temperature and material temperature.

30

When the temperature of the material corresponds to the water boiling point, the gas will consist substantially of steam from part of the vaporised water content of the material.

- 5 In addition to containing air or inert gas followed by air or inert gas and steam and finally steam, the gas taken from the main loop into the sub-flow loop also contains the contaminating substances that are present, these substances being expelled from the material in vapour form and enriched  
10 in the gas by co-distillation with water or by steam distillation. This takes place during all phases of the process and is governed by the properties of said substances; low-boiling point substances are driven off at lower temperatures than high boiling substances. Consequently, the  
15 gas taken into the sub-flow loop can contain different types and concentrations of expelled substances as a function of primarily the process temperature and the degree of enrichment (saturation) in the gas.
- 20 Water co-distillation enables some of the high molecular and high boiling contaminating substances present to be vaporised and driven-off and enriched in the gas already at low temperatures, e.g. at the boiling point of water.
- 25 At a process temperature corresponding to the boiling point of water, the gas is comprised of steam and expelled contaminating substances. When all moisture in the material has been vaporised by the hot, recirculating steam in the main loop, the temperature of the material rises to above the  
30 boiling point of water and reaches the temperature required for remaining contaminating substances to be vaporised and driven from the material. The temperature is adjusted to the



requisite level, by heating the steam with a heating unit as the steam is recycled within the main loop to the material.

5 No fresh steam will be generated for removal to the sub-flow loop when the material is dry, which means that the expelled contaminating substances can be enriched to a still greater extent in the steam recirculating in the main loop than during vaporisation of the moisture in the material. A small part of the steam in the main loop is, however, taken out in 10 the sub-flow loop while increasing the temperature, so as to compensate for the increase in volume resulting from said temperature increase.

The material is treated with gas at a temperature 15 corresponding to the boiling point of the contaminating substance and at atmospheric pressure or at a pressure as close to atmospheric pressure as that permitted by the technical aspects of the process.

20 Water is injected into the main loop in order to enable steam and enriched contaminating substances to be taken out in a controlled manner during the high temperature phase, i.e. when steam is no longer produced from vaporised moisture in the material. Vaporisation of the water results in a volume 25 increase in the main loop, which is compensated for by taking a corresponding volume into the sub-flow loop. Thus, a determined volume of steam containing enriched contaminating substance can be taken from the main loop to the sub-flow loop, by injecting a determined volume of water into the main 30 loop.

Gas taken out from the main loop into the sub-flow loop is led to a second separation process for separation of the enriched contaminating substances from the gas, whereafter the gas is either circulated back to the main loop or removed from the system.

#### The second separation process

Subsequent to being driven-off, the substances are separated from the gas in a second separation process in a sub-flow taken from the main flow, said separation being effected in one of three different ways: combustion, complete or partial adsorption on a contaminant-selective substance, separation after cooling and condensing the gas, or in different combinations of these three processes. The method or process chosen will depend on the number, type(s) and concentrations of the enriched contaminating substances.

Separation can be effected from the very start of the enrichment of respective substances in the gas until these substances have reached their respective "saturation consistencies" in the recirculating gas.

#### *1 Separation by combustion*

One method of separation is to destroy contaminating substances in a sub-flow taken from the main flow by combustion directly in the gas. This presumes that the substance concerned is combustible, i.e. a hydrocarbon compound. Destruction is effected by causing the gas containing said substance to pass a combustion unit, wherewith the substance is combusted (oxidised) and

decomposed to water vapour and carbon dioxide and also to gaseous chlorine in the case of chlorinated hydrocarbons. When chlorinated hydrocarbons are combusted, chlorine (probably in the form of chlorine gas) can be separated from the gas by causing the gas to pass a chemical substance downstream of the combustion unit, a chlorine-selective sorbent (see below) which adsorbs/absorbs and binds the chlorine as the gas passes therethrough.

- 10 The combustion unit is comprised of a burner, a catalyst or a burner-catalyst combination. Thermal energy is generated in conjunction with the combustion of the contaminating substances. One advantage with this method is that thermal energy is generated at the same time as the substances are destroyed and can be recovered and used directly in the process, by delivering said energy to the first separation process through the medium of a heat exchanger. Another advantage is that there is no need for either sorbent or the recovery of concentrates of contaminating substances (see below) obtained by sorbent regeneration.

Maximum destruction of contaminating substances in the gas can be achieved by recirculating the gas several times through the combustion unit.

- 25 The thermal energy released in the combustion process is transferred to the gas in the main loop through the medium of a heat exchanger.

- 30 The gas can then be returned to the process or removed from the system. Gas that is removed from the system is cooled to a temperature beneath the boiling point of water and the

water condensate and non-condensable gases are passed through chemical filters adapted for adsorbing or absorbing any contaminating substance rests. The water condensate is then returned to treated material and the gas released to the surrounding atmosphere.

## *2 Separation after cooling and condensation of the gas*

Another way of separating contaminating substances in a sub-flow is to cool the gas to a temperature beneath the boiling point of water whereafter the substances are extracted conventionally from the resultant water condensate and non-condensable gases with the aid of a chemical filter (e.g. activated carbon) capable of adsorbing/absorbing and binding the contaminating substances directly from the non-condensable gas and the water condensate respectively.

Rests of contaminating substances can also be separated from the water condensate and the non-condensable gas respectively by precipitation, etc.

Enrichment of the contaminating substances in the gas during the first separation process in the main loop will mean that the gas taken from the main loop and cooled/condensed will contain the substances to a corresponding high level of enrichment in the water condensate and/or the non-condensable gas. This represents a considerable advantage both from a technical and an economical aspect in comparison with those methods in which steam is condensed after having passed once through the contaminated material.

The water condensate is returned to the treated material and the gas is released to the surrounding atmosphere.

3      *Separation with the aid of substance selective chemical*  
5                    *substances*

A third method of separation, where the contaminating substances are not destroyed directly in the gas or cooled with the gas in accordance with the foregoing, involves  
10 separating enriched contaminating substances in a sub-flow, by allowing the gas to pass a substance-selective chemical substance which is chosen and adapted to adsorb/absorb the contaminating substance or group of contaminating substances from the gas or to extract the substance or substances  
15 chemically in some other way.

Maximum separation of contaminating substance from the gas can be achieved, by recirculating the gas to the contaminant-selective chemical substance several times. Different  
20 enriched contaminating substances or groups of such substances present in the gas can be separated from the gas selectively, by passing the gas through two or more such chemical substances in series.

25 The chemical substances belonging to one group type (so-called sorbents) are characterised in that they absorb (adsorb) and bind enriched contaminating substance from the gas in a non-destructive fashion. The chemical substances of another group type, so-called dehalogenating sorbents are  
30 characterised in that they take-up enriched chlorinated hydrocarbon compounds, e.g. PCB (polychlorinated biphenyl), from the gas at the same time as the chlorine bonds are

broken and the chlorine atoms released: The biphenyl part of the PCB-molecule is taken up and bound to the chemical substance whereas the chlorine atoms are released and accompany the gas. The released chlorine (probably as gaseous chlorine or some other gaseous chlorine compound) can then be taken up on another chemical substance that is chlorine selective as the gas passes through.

The gas can then be returned to the process or removed from the system. Gas that is removed from the system is cooled to a temperature beneath the boiling point of water, whereafter the water condensate thus formed and non-condensable gases respectively pass through chemical filters adapted for taking up any rests of the contaminating substances. The water condensate is then passed back to treated material and the gas released to the surrounding atmosphere.

4     *Combination of the separation methods according to 1-3 above*

20

These separation methods can be applied either individually or in combination with each other. This latter case applies when the material is combined with two or more types of substances or groups of substances that cannot be separated from the gas with one and the same separation method, as is often the case.

**EXAMPLE**

30     An example relating to the separation of a plurality of contaminating substance from a contaminated material will now be described with reference to Fig. 1 and to Figs. 2-6. It is

assumed that a material (e.g. soil) is contaminated with several different contaminating substances or groups of contaminating substances, designated A-E (Fig. 1), where each behave differently in the treatment process, i.e. are expelled from the material at different temperatures, have different properties and/or form decomposition products such that they must be separated from the gas in different ways.

Substance A is expelled during the heating phase, substance B and (partially) substance C are expelled during the drying phase, and substances D and E are expelled during the high temperature phase. This example has been simplified for the sake of illustration; in reality many of these different substances are expelled over much broader temperature intervals that significantly overlap one another. This means that the different separation methods are used simultaneously during the process, for instance by passing the gas containing the enriched contaminating substances in said sub-flow loop to, e.g., a unit which accommodates one type of contaminate-selective sorbent, and thereafter to a combustion unit, or vice versa, in order to shift to, e.g., another type of chlorine-selective sorbent or contaminate-selective sorbent later on in the process.

The process flows may remain unchanged in practice, during the whole of the process; the gas flow passes continuously through different separation units in series; these units fulfil their respective functions as the gas entrains the contaminating substances or decomposition products which the units are designed to separate from the gas, during the course of the process.

The process comprises three phases: the heating phase at a temperature up to 100°C, a drying phase conducted at a temperature of 100°C, and a high temperature phase conducted at a temperature of 500°C in the present example.

5

Substance A     Metallic (elementary) mercury, Hg.

Metallic Hg is volatile and is expelled in vapour phase quickly from contaminated material already at temperatures beneath 100°C, i.e. the heating phase (see Fig. 1). Hg cannot  
10 be destroyed and must therefore be separated directly from the gas with the aid of an Hg-selective chemical substance (sorbent).

Substance B     Light weight - average weight petroleum  
15 hydrocarbons

This substance is actually a substance group consisting of aromatic and/or aliphatic hydrocarbons that depart successively at a temperature of about 100°C, i.e. during the drying phase. The lighter substances are expelled first and  
20 are followed by the substances of average weight for destruction by combustion.

Substance C     Average weight - heavy hydrocarbons.  
This is a substance group consisting of aliphatic  
25 hydrocarbons that depart successively at a temperature of about 150-200°C, i.e. during the high temperature phase. The substances are destroyed by combustion.

Substance D     PCB  
PCB is a collective term for an aromatic hydrocarbon group  
30 consisting of a biphenyl group of different chlorine contents constituting a plurality of so-called PCB-congeners; this chlorine is released when the PCB-molecule is decomposed. The



heaviest and structurally "flattest" of the PCB-congeners are expelled from the material at 250-300°C.

PCB can be destroyed by combustion, wherewith chlorine  
5 constitutes one of the decomposition products. PCB can also  
be taken up by PCB-selective chemical substances, either a  
PCB-selective sorbent that takes-up and binds the PCB-  
molecule, or a so-called dehalogenating sorbent that takes up  
10 the biphenyl group of the PCB-molecule but releases the  
chlorine atoms of said PCB-molecule. The chlorine generated  
by combustion and when using a dehalogenating sorbent can  
then, in turn, be taken-up by a separate chlorine-selective  
chemical substance (sorbent).

15 Substance E Mercury in the form of mercury sulphide, HgS.  
HgS is a solid compound (and a naturally occurring Hg  
mineral) and formed in Hg-contaminated soil from metallic Hg  
and sulphur. In order to separate Hg, it is necessary to heat  
the material to a temperature of about 500°C; this  
20 temperature can be lower under certain conditions. The  
compound is therewith decomposed and Hg is driven off as  
(probably) metallic Hg, which is separated directly from the  
gas with an Hg-selective chemical substance (c.f. substance A  
above).

25  
In this example, the contaminated material is a "normal"  
moraine soil containing 10-20% water. The various substances  
A-E will be driven-off successively as the material is heated  
from its initial temperature up to the highest process  
30 temperature of 500°C.

As the substances are expelled from the material, they are  
separated from the gas in the sub-flow loop by the selected

separation methods, i.e. by combustion and by a selective chemical substance respectively, or by combinations of these methods. The substances can be separated by causing the gas to pass a sorbent and a combustion unit in succession (or vice versa), or by passing the gas to the mercury-selective sorbent during the process-temperature interval at which mercury is expelled from the material, or by passing the gas to the combustion unit during the process-temperature interval in which the petroleum products are expelled from said material.

As illustrated in Fig. 2, the process involves the continuous expulsion and enrichment of the contaminating substances in a main flow in the main loop 23, and also involves taking-out a sub-flow in a sub-flow loop 27 for separating enriched substances from the gas (this sub-flow may be taken-out continuously or periodically, depending on the process phase concerned - see above).

In accordance with Fig. 5, the process is effected in a gas-recirculating main loop 23 and a sub-flow loop 272 having a unit 28 which includes a mercury-selective substance. Contaminated material is fed into a closed process container 20 at 21, said container including a particle filter 201. The air present in the system begins to circulate in the closed main loop 23, assisted by a fan or blower 24, and is heated continually by a heating unit, heat exchanger 26, prior to its passage to and through the process container 20.

The material is therewith heated successively and the moisture in the material begins to vaporise. At 70-80°C, more than half of the air present in the main loop has been

replaced by water vapour. A significant part of substance A is expelled to the gas in the main loop 23.

5 If the material contains volatile contaminating substances, which may present a risk of gas explosion during heating in the presence of oxygen, the air (actually the oxygen content of the air) is replaced completely or partially with an inert gas before heating commences.

10 A sub-flow of process gas (air or inert gas and later water vapour or steam) is taken from the main loop 23 and passed into the sub-flow loop 272. This sub-flow is created automatically with the aid of suitable valve means that opens in response to an increase in pressure and volume in the main  
15 loop. The expelled and enriched contaminating substances A are therewith taken-out with the gas and conducted in the sub-flow loop 272 to the unit 28 that contains the mercury-selective substance, where mercury present in the gas is taken-up and bound while the gas passes through said  
20 substance and the gas is either returned to the main loop 23 or removed from the system via the units 29, 291, 292 for gas cooling and gas condensing, and cleaning of the water condensate and non-condensable gas respectively.

25 When a temperature of 100°C has been reached, the substance A will have been expelled and taken-out into the sub-flow loop 272 where it is taken-up by the mercury-selective sorbent 28 and all air or inert gas in the main loop 23 has been replaced by the steam generated by the vaporisation of  
30 moisture in the material. The mercury-containing sorbent is removed for regeneration, wherewith the mercury is obtained as a concentrate and the sorbent is reused in the separation

process. The sorbent may alternatively be of a disposable kind, i.e. a sorbent that is removed from the process for final treatment together with the mercury and replaced with a new and unused sorbent substance.

5

The process now takes place in accordance with the Fig. 3 illustration, in the gas recirculating main loop 23 and in a sub-flow loop 271 comprising a unit 25 that includes a combustion unit consisting of a burner and/or a catalyst.

10

Expulsion of substance B begins. The steam generated by the moisture present in the material is taken-out together with the expelled substance B continuously from the main loop 23 and passed to the sub-flow loop 271 and the combustion unit 25. Substance B is destroyed and the thermal energy released is transferred to the gas in the main loop 23 via the heat exchanger 26 connected downstream of the combustion unit. The gas and formed decomposition products, steam and carbon dioxide, are then passed to the unit 29 for gas-cooling and gas-condensation, whereafter the water condensate (from the steam) and non-condensable gas (carbon dioxide) are passed to respective cleansing units 291 and 292.

15

20

If the material is dry initially, steam cannot be generated internally from moisture present in the material during the heating process. In this case, water is injected into the main loop 23 from an external source through the water injector 230, and then vaporised to therewith "artificially" generate steam for replacement of air or inert gas.

25

30

When the material in the process container 20 has dried out during the continued process, the substance B will have been

expelled and combusted. Steam is no longer generated by heating the material. Heating of the material to a temperature above the boiling point of water now commences. The process remains set in accordance with Fig. 3, where  
5 similar to substance B the substance C is comprised of combustible hydrocarbons.

Because volume, and therewith pressure, increases in the main loop during this rise in temperature, a certain, but limited,  
10 amount of steam and substance C will be taken from the main loop into the sub-flow loop.

However, the major part of the steam in the main loop 23 recirculates through the material as the temperature of the  
15 material rises and successively more contaminating substance C is expelled and enriched in the steam. When a determined volume of water is injected into the main loop through the water injector 230 upstream of the heating unit, i.e. the heat exchanger 26, this water will be vaporised to provide a  
20 specific volume of steam which results in an increase in volume in the main loop 23 and therewith an automatic take-out of a corresponding volume of steam into the sub-flow loop 271.

25 This enables the sub-flow of steam-enriched contaminating substance C from the main loop to be controlled and taken out with enriched concentrations in the steam suitable for the combustion process.

30 Substance C has now been expelled. The process temperature continues to rise. The process is set in accordance with Fig. 5 or Fig. 6, depending on circumstances; both process

settings enable substance D to be separated from the gas (the steam). Expulsion of substance D from the material now commences and substance D is enriched in the gas in the main flow 23. Sub-flows of the gas and substance D are taken from the main loop 23 into the sub-flow loop 271 for separation of substance D from the gas, by injecting water through the injector 230.

According to Fig. 5, the sub-flow loop includes a contaminant-selective substance, in this case a PCB-selective sorbent. The sorbent may comprise liquid polyethylene glycol (PEG) or polypropylene glycol (PPG), which both effectively take-up and bind substance D, i.e. PCB, from the steam. Alternatively, the sorbent may comprise a so-called dehalogenating sorbent, e.g. a polyethylene glycol that contains alkali metal (APEG) or a polypropylene glycol that contains alkali metal (APPG). These sorbents take-up substance D while, at the same time, breaking the bond between the biphenyl group and the chlorine in the PCB-molecule; the biphenyl group is bound to the sorbent while the chlorine remains in gas form as chlorine gas or some other chlorine compound.

The gas and the chlorine gas are led further to a unit that includes a chlorine-selective sorbent which takes-up and binds the chlorine as the gas passes therethrough, said gas being returned to the main loop 23 or is removed from the system via the gas-cooling and gas-condensing unit 29 and the water-condensate cleansing unit 291. Because the gas consists of steam, no cleansing or release of non-condensable gas takes place.

The sorbent is regenerated, wherewith the biphenyl group is obtained as a concentrate for recovery and the sorbent is reused in the separation process. The sorbent may alternatively be of a disposable nature, in which case it is removed from the process and handled together with the biphenyl group and replaced with a new, unused sorbent substance.

According to Fig. 6, the sub-flow loop includes a combustion unit 25 and a unit 28 that contains a contaminant-selective substance consisting of a chlorine-selective sorbent. The sub-flow of gas and enriched contaminating substance D is first led to the combustion unit 25, wherein the substance D is decomposed to steam, carbon dioxide and chlorine gas or some other gaseous chlorine compound. The thermal energy thus generated herewith is returned to the main loop 23 by the gas via the heat exchanger 26.

The gas and the decomposition products are then led to the chlorine-selective sorbent 28 which takes-up and binds the chlorine as the gas passes through said sorbent, said gas being removed from the system via the gas-cooling and gas-condensing unit 29 and the units for cleansing the water condensate and the non-condensable gas respectively.

The process temperature increases continuously. Substance D has now been driven-off. The process is again set in accordance with Fig. 5, with a unit that contains a mercury-selective sorbent (of the same kind as that used to take-up substance A).

The process temperature rises to the temperature interval in which substance E present in the material, i.e. mercury sulphide,  $\text{HgS}$ , decomposes thermally, wherewith released (probably) metallic mercury is driven-off and enriched in the gas in the main loop. Water is injected into the main loop 23 so as to enable a suitable flow of mercury-containing gas to be taken from the main loop 23 and into the sub-flow loop 272, said gas flow being cooled (although not beneath the boiling point of water) and passes the mercury-selective sorbent, which takes-up the mercury as the gas passes therethrough. The gas is either returned to the main loop 23 or is removed from the process via the gas-cooling and gas-condensing unit 29 and the subsequent unit 291 containing a chemical purification filter for filtering the water condensate.

Expulsion of the substance E finalises the treatment of the material and the process is therewith terminated. Water is fed into the system so as to dilute the gas in the main flow, whereafter the system is emptied. The material is cooled with gas and/or water. The energy thus generated can be recovered and conducted to another process container in which a corresponding process is ongoing, and the cooled material is discharged from the container at 22. The container is filled with fresh contaminated material and the process repeated.



## CLAIMS

1. A method of separating contaminating or polluting substance, e.g. chemical substances such as PCB, dioxins, aliphatic and aromatic substances in creosote, oil and other petroleum compounds, and other chemical substances having similar chemical and physical properties as the first-mentioned chemical substances, and distillable metals such as mercury and distillable compounds of such metals, from material contaminated with the contaminating substance, **characterised** by heating the contaminated material in a first separation process and treating said material with a circulating gas which is caused to pass through the material repeatedly in a closed circuit, a main loop (23), during the process while increasing in temperature up to the boiling point of the contaminating substance, so that the contaminating substance present in said material will be expelled successively from the material and enriched in vapour phase in the circulating gas, and by separating the thus expelled and enriched contaminating substance in a sub-flow loop (27) in a second separation process.

2. A method according to Claim 1, **characterised** by returning any thermal energy released during the second separation process to the closed circuit (23) and therewith to the first separation process.

3. A method according to Claim 1, **characterised** in that the contaminated material is heated with gas by heating air present in the main loop (23) by means of a heating unit and causing the gas to circulate in said loop with the aid of a fan or blower (24), wherewith water present in the

contaminated material is successively vaporised; in that air, steam and expelled and enriched contaminating substance are taken into the sub-flow loop (27) when the gas pressure in the main loop has reached a predetermined value; and in that  
5 when all air has been removed from the main loop (23) and the contaminated material is dry, steam and contaminated substance enriched in said steam are taken from the main loop to the sub-flow loop (27) by injecting water into said main loop, said water being vaporised during continued heating by  
10 means of the heating unit.

4. A method according to Claim 3, **characterised** by replacing oxygen in the air present in the main loop (23) with inert gas.

15

5. A method according to any one of Claims 1-3, **characterised** in that in the second separation process in the sub-flow loop (27), the gas and enriched vaporised contaminating substance are caused to pass through a  
20 separation unit that includes a combustion unit (25) for decomposition of said contaminating substance.

6. A method according to Claim 5, **characterised** in that in the second separation process, the gas and enriched gaseous  
25 substance are caused to pass the separation unit in the sub-flow loop (27) where said combustion unit (25) consists of a burner and a catalyst.

7. A method according to Claim 5, **characterised** in that in  
30 the second separation process in the sub-flow loop (27), the gas and enriched gaseous substance are caused to pass through

the separation unit where the combustion unit (25) is comprised of a burner.

8. A method according to Claim 5, **characterised** in that in the second separation process in the sub-flow loop (27), the gas and enriched gaseous substance are caused to pass through the separation unit where the combustion unit (25) is comprised of a catalyst.

9. A method according to Claim 5, **characterised** in that decomposition products and the gas prior to exiting from the process are caused to pass through a separation unit that includes a chemical substance which is chosen and adapted to separate decomposition products from the gas.

10. A method according to Claim 1, **characterised** in that in the second separation process in the sub-flow loop (27), the gas and gaseous contaminating substance are cooled and said contaminating substance then separated from the resultant water condensate and non-condensable gas.

11. A method according to Claim 1, **characterised** in that in the second separation process in the sub-flow loop (27), the gaseous contaminating substance and said gas are caused to pass through a separation unit that includes a contaminant-selective chemical substance (28) chosen and adapted for separating a contaminating substance from the gas, whereafter the gas is removed from the system.

12. A method according to Claim 1, **characterised** in that in the second separation process in the sub-flow loop (27), the gaseous contaminating substance and the gas are caused to

pass through a separation unit that includes a contaminant-selective chemical substance (28) which has been chosen and adapted to separate a contaminating substance from the gas, whereafter the gas is returned to the main loop (23).

5

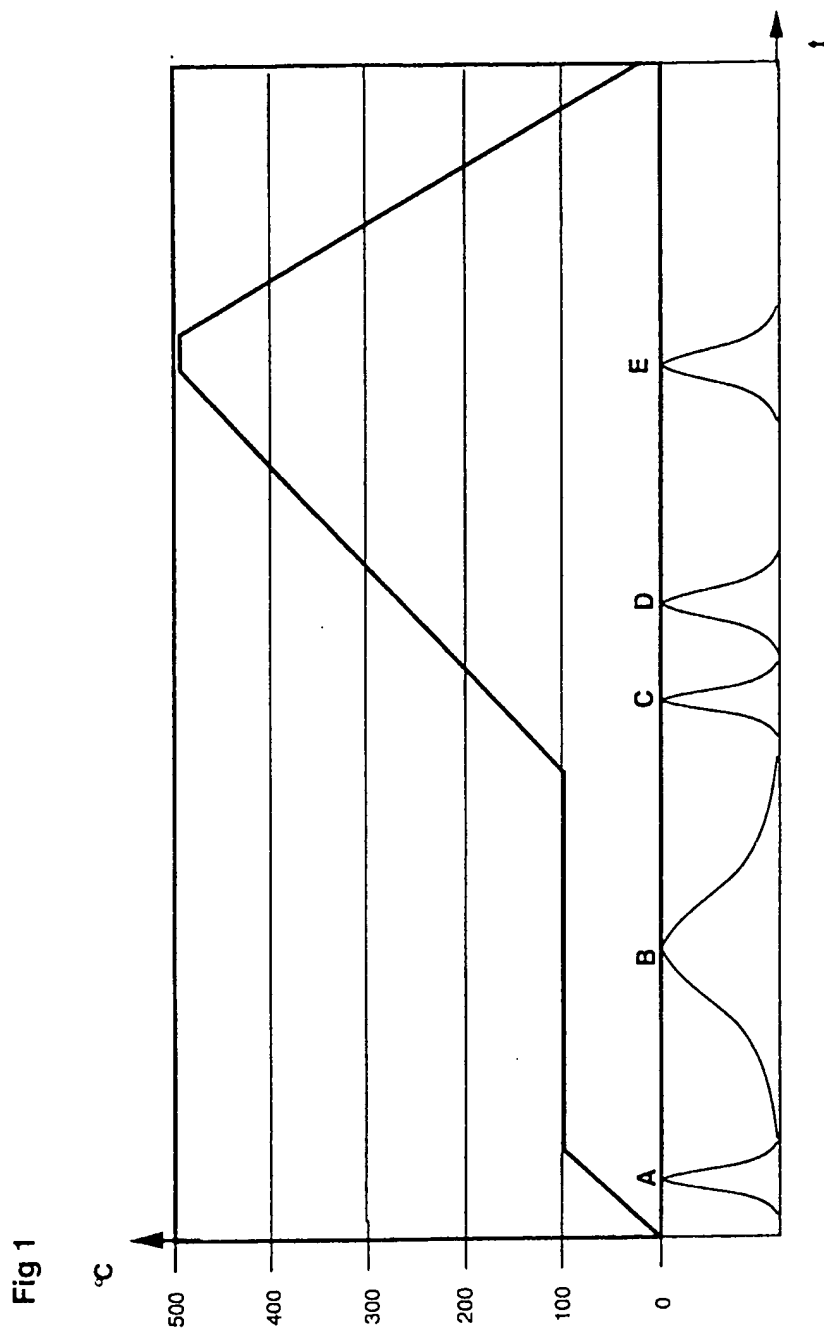
13. A method according to Claim 1, **characterised** in that in the second separation process in the sub-flow loop (27), the gaseous contaminating substance and the gas are caused to pass through a separation unit that includes a contaminant-selective chemical substance (28) which has been chosen and adapted to decompose a contaminating substance in the gas and to take-up part of the decomposed contaminating substance.

10

14. A method according to Claim 13, **characterised** in that subsequent to passing the separation unit that includes said contaminant-selective chemical substance (28), the gas and formed decomposition products are passed to a second separation unit that includes a chemical substance which has been chosen and adapted to take-up formed decomposition products from the gas.

15

20





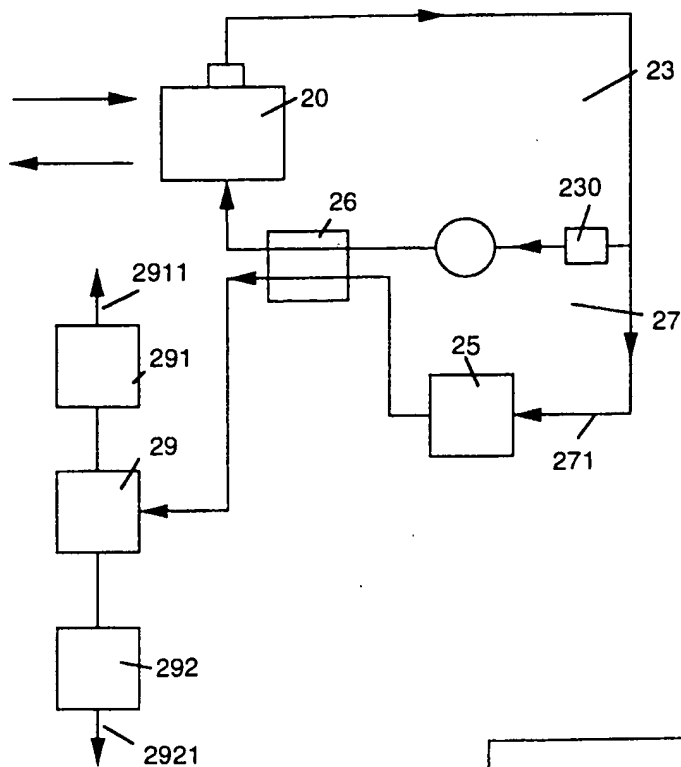


Fig 3

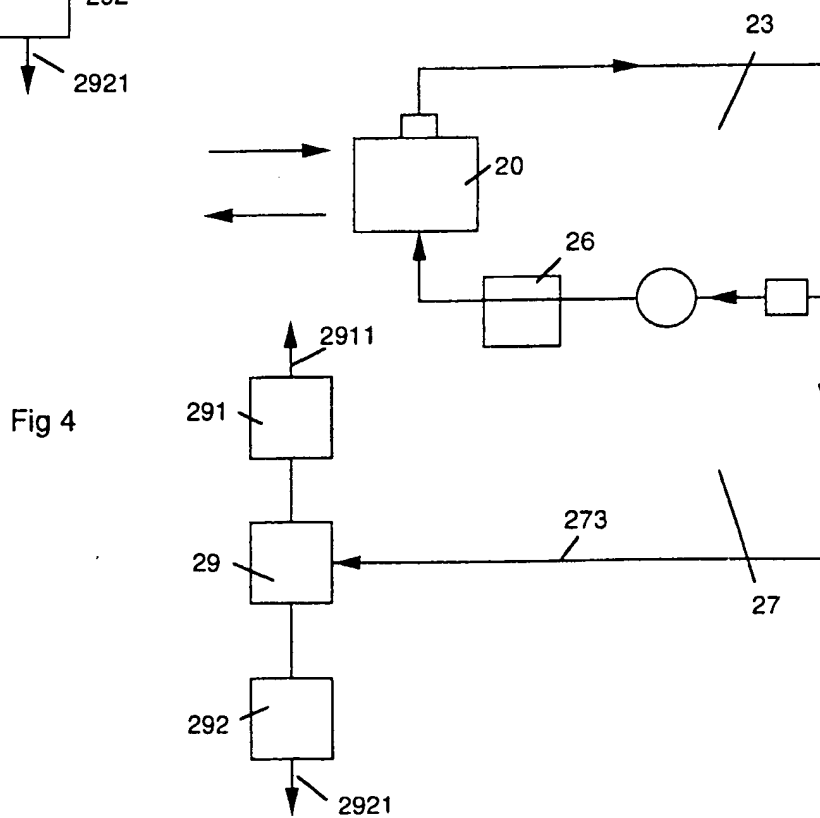


Fig 4

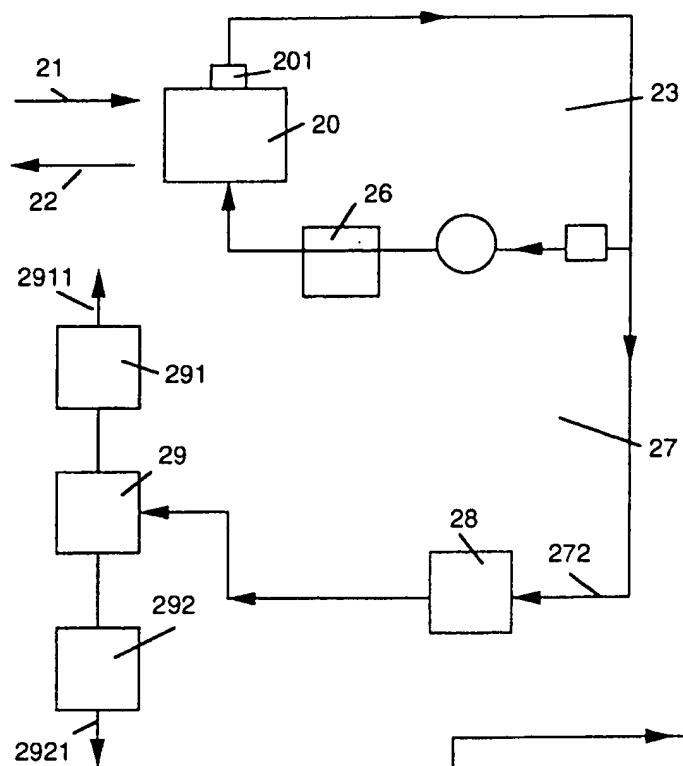


Fig 5

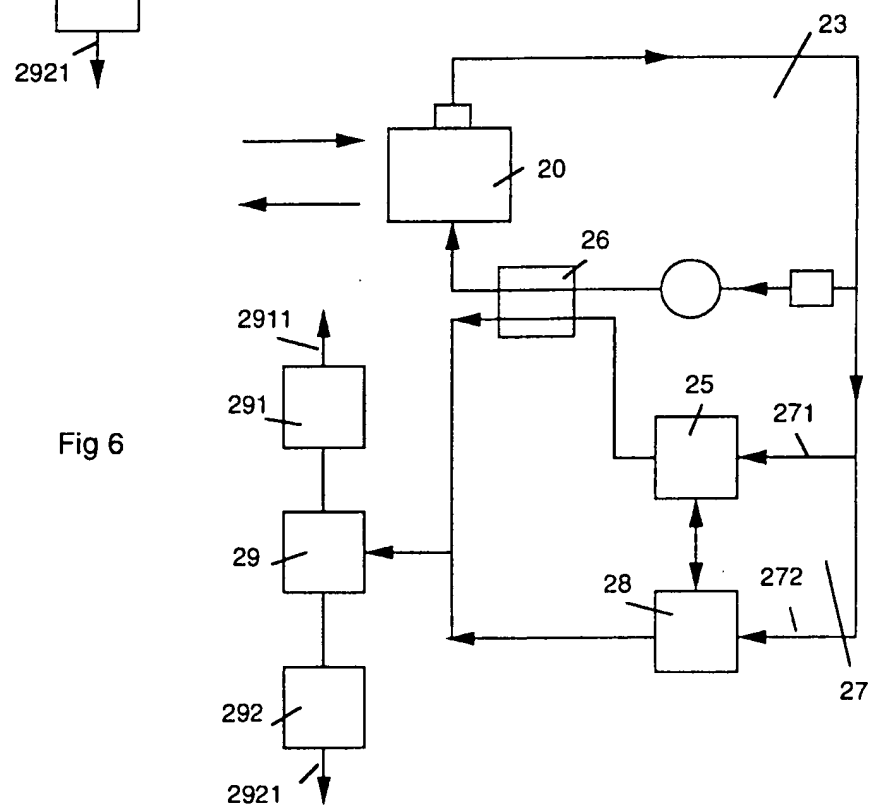


Fig 6



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 98/01395

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC6: B09C 1/00, B01D 1/00, F26B 3/06 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC6: B01D, B09C, F26B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
SE,DK,FI,NO classes as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
QUESTEL; EDOC, WPIL, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5172709 A (BART J. ECKHARDT ET AL), 22 December 1992 (22.12.92), column 5, line 8 - column 11, line 2, figure 2  --	1-14
A	EP 0715902 A1 (KETTENBAUER, FRANZ ET AL), 12 June 1996 (12.06.96), page 4, line 8 - page 5, line 58, figure 1  --	1-14
A	DE 4226584 A1 (GRADL, TONI), 17 February 1994 (17.02.94), column 2, line 46 - column 3, line 15, figure 1  -- -----	1-14
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
20 October 1998		03-11-1998
Name and mailing address of the ISA Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86		Authorized officer Bengt Christensson Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

27/07/98

International application No.  
PCT/SE 98/01395

Patent document cited in search report			Publication date	Patent family member(s)	Publication date
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EP	0715902	A1	12/06/96	NONE	
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DE	4226584	A1	17/02/94	NONE	
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